PA NT COOPERATION TREA

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

FORSLUND, Niklas
Pharmacia & Upjohn AB
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SUÈDE

Date of mailing (day/month/year)
18 April 2001 (18.04.01)

Applicant's or agent's file reference
1861-PCT/2

IMPORTANT NOTIFICATION

International application No.
PCT/EP00/02539

International filing date (day/month/year)
16 March 2000 (16.03.00)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

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2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [X] the name [ ] the address [ ] the nationality [ ] the residence

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3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
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Woorl

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PCT

REC'D 20 MAR 2001
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70) 14

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
1861-PCT/2		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP00/02539	16/03/2000	16/03/1999
International Patent Classification (IPC) or national classification and IPC C08F8/00		
Applicant PHARMACIA [& UPJOHN] GRONINGEN BV et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of / sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08/10/2000	15.03.01
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Boonen, J Telephone No. +49 89 2399 8513

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/02539

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:
Description, pages:

1-24	as originally filed				
Claims, No.:					
5 (part),6-32	as originally filed				
1-4,5 (part)	as received on	26/04/2000	with letter of	25/04/2000	

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:
   - ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-32
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-32
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

2. Citations and explanations
   see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The present claims 1 to 32 are not novel contrary to the requirements of Article 33(2) PCT.
   Document D1 WO-A-9 908 135 discloses (loc. cited in the Search Report) a composition which is cured using benzoylphosphine oxide photoinitiator.
   The composition can be made of polyethylene oxide mono- and dimethacrylates and acrylates.

2. Also document D2 JOURNAL OF APPLIED POLYMER SCIENCE (loc. cited in the Search Report) discloses the use of benzoyldiphenylphosphinoxide for curing.

3. The present claims 1 t o 32 do also not show the presence of inventive step as required by Article 33(3) PCT.
   Documents D1 and D2 demonstrate that benzoylphosphine oxide can be used for curing substituted ethylene polymers.

Claims

1. Macromolecular photocrosslinkers having a general formula

$(A)_n(B)_m(C)_p$, wherein

(i) A, B and C are units of substituted ethylene or siloxane groups in the macromolecular structure;

(ii) C carries a photoactive groups;

(iii) n = 0-98 mole %, m = 0-98 mole %, n+m = 50-98 mole % and p = 0.5-50 mole %;

and when said photoactive groups are exposed to light of determined wavelengths above 305 nm, radicals are generated and retained on the macromolecular photocrosslinkers and reacting so as to accomplish a crosslinked network structure.

2. Photocrosslinkers according to claim 1 characterized in that said photoactive group comprises a phosphine oxide.

3. Photocrosslinkers according to claim 2 characterized in that the photoactive group is an acyl- or aroyl phosphine oxide.

4. Photocrosslinkers according to claim 3 characterized in that the photoactive group is linked to the ethylene groups of units C by a linking group comprising a phenylene group, said phenylene group being optionally substituted.

5. Photocrosslinkers according to claim 1, wherein the ethylene units A, B, C of the macromolecular structure comprises substituents in accordance with:

A= $-CH_2-C(R^1R^2)-$, B= $-CH_2-C(R^1R^3)-$, C= $-CH_2-C(R^1R^4)-$, wherein

09/936647

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 September 2000 (21.09.2000)

PCT

(10) International Publication Number
WO 00/55212 A1

(51) International Patent Classification[7]: C08F 8/00, C08G 77/38, G02B 1/04

(21) International Application Number: PCT/EP00/02539

(22) International Filing Date: 16 March 2000 (16.03.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9900935-9 16 March 1999 (16.03.1999) SE

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(81) Designated States *(national)*: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(48) Date of publication of this corrected version:
20 September 2001

(15) Information about Correction:
see PCT Gazette No. 38/2001 of 20 September 2001, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/55212 A1

(54) Title: MACROMOLECULAR COMPOUNDS

(57) Abstract: The invention relates to macromolecular photocrosslinkers having polymeric backbones of substituted ethylene or substituted siloxane groups carrying photoactive groups. The photocrosslinkers are capable of producing, when being exposed to light of determined wavelengths above 305 nm, radicals which are retained on the macromoleculecular photocrosslinkers and reacting so as to accomplish a crosslinked network structure. The invention further relates to the use of the photocrosslinkers in different systems and their utility in production of medical devices including ophthalmic lenses.

Macromolecular compounds

Field of invention

The present invention relates to new photoinitiators capable of acting as photocrosslinkers providing a combination of photoinitiating and crosslinking processes.

Background of invention

The UV curing of resin formulations is widely used in industry as the setting process for coatings, adhesives, and more recently paints. Such formulations may comprise a combination of vinyl, usually acrylate, monomers and crosslinkers, together with a photoinitiator. Other possible constituents of the formulations include crosslinkers and vehicles. In general an advantage of photocurable formulations is that the monomers act as their own vehicle, and the use of solvent is obviated, which has environmental advantages.

Advances in the technology of photocuring, improvements such as, those in UV lamps, cationic initiators for epoxide-based formulations, water borne coatings, and many novel monomers has enabled this production process to penetrate a number of important manufacturing sectors. Photopolymerization is now used in photoresists for printed circuits and microelectronics, for photolithography, magnetic recording media, glass-fiber laminates, and for medical devices, especially for dental and ophthalmic applications.

For the medical applications of photopolymerisation it is usual to employ visible light, rather than UV, to effect the cure of the resin formulation. The use of visible, usually blue, light avoids exposing patient and dentist or surgeon to harmful irradiation. Increasingly the merit of this approach is being recognized for industrial practice, where operatives also need protection from prolonged exposure to harmful UV.

European Patent 0800 657 describes a photoinitiator linked to a macromer structure which together with a copolymerizable monomer and a crosslinker is capable forming a polymerization product, such as an ophthalmic lens that retains photoinitiator radical in

the resulting network. This is advantageous in medical applications wherein such potentially harmful radicals must be carefully controlled. However, this system would not be applicable for producing a polymerized product directly in the capsular bag in the eye since it is not directed to photoinitiators activated by light in the visible range. US Patent No. 4,536,265 discloses siloxane polyphotoinitiators to be used with a curable silicone resin. This system is UV curable and consequently it will not be applicable for photocuring in the living eye.

It is a characteristic of almost all, if not all, of the formulations used for aforementioned types of application that they are crosslinked. Crosslinking of the polymeric bases which constitute the coatings or artifacts of the aforementioned industrial products confers important advantages upon them. Crosslinked polymers have greater environmental (e.g. temperature and moisture) resistance, solvent resistance and dimensional and mechanical stability, than equivalent linear polymers. This is especially so for where the equivalent linear polymer are produced by photopolymerisation they have an atactic, non-crystalline, structure.

Crosslinking is introduced into photopolymerized products by including in the formulation for the resin, coating or gelling system, an acrylate, or similar, crosslinker, which is characterized by having two or more crosslinkable acrylate or vinyl functions. In some formulations this crosslinking species is a polymer of low molecular weight. The crosslinker copolymerizes with the monomers of the formulation to produce a network structure.

It is the object of the present invention provide compounds which act as photocrosslinkers for vinyl, acrylate and methacrylate monomers and acrylated silicone compositions, especially in solution.

It is also an important object of the present invention to provide photocrosslinkers with capability to act in aqueous solutions, especially on water soluble macromolecular particles having functional groups for crosslinking.

It is another object of the present invention to provide photocrosslinkers with enhanced photoactivity (100 % conversion of monomer to polymer in aqueous solution) which reduces photoinitiator residues to a minimum, especially, vinyl modification of

photoinitiator component and thereby reducing compositional drift, Draize and other environmental hazards.

The invention as presented below will explain how the mentioned objects are met while discussing further obvious advantages.

Description of the invention

The present invention pertains to macromolecular hydrophilic photocrosslinkers having a general formula $(A)_n(B)_m(C)_p$, wherein

(i) A, B and C are units of substituted ethylene or siloxane groups in the macromolecular structure;

(ii) A, B and C are randomly distributed and the unit C carries a photoactive group;

(iii) n = 0-98 mole %, m = 0-98 mole %, n+m = 50-98 mole % and p = 0.5-50 mole %.

When the photoactive groups of units C are exposed to light of determined wavelengths above 305 nm, radicals are generated which are retained on the macromolecular photocrosslinkers and will react to form a crosslinked network structure. Preferably the final structure is solid article.

The photocrosslinker further preferably further comprises functional groups for crosslinking. Such groups are conventionally vinylic, acrylic or methacrylic groups and their nature and introduction on polymeric backbone are well known to persons skilled in the art and will be referred to as "functional groups for crosslinking".

According to one aspect of the invention a fluid composition of the photocrosslinker in a suitable amount can be directly crosslinked into the final solid product upon sufficient irradiation. In another aspect the composition for crosslinking into a solid article comprises suitable amounts of the photocrosslinker and a polymer carrying functional groups for crosslinking. The photocrosslinker in such a system will thereby replace the conventional combination of crosslinker and photoinitiator. Applicable polymers with suitable functional can readily be provided with the skilled person for the purpose of crosslinking desired articles. For example it would be

conceivable to employ polymers having a sufficiently high refractive index to be acceptable as intraocular lenses. Suitable polymers can be, for example, be found in International Patent Application PCT/EP99/07718. In a still another aspect of the present invention, the photocrosslinkers can be employed in a composition, preferably an aqueous composition further comprising at least one copolymerizable vinylic, acrylic or methacrylic monomer. Such monomers and combinations thereof are well known in the art and will not be described herein in further detail. It is, however, to be understood that the photocrosslinker will replace conventional crosslinking agents and their combination with photoinitiators in such systems.

It is highly preferred that the photoactive groups of the photocrosslinkers comprise a phosphine oxide, in order to generate the necessary radicals for crosslinking from the exposure of visible light. More preferably, the photoactive group is an acyl- or aroyl phosphine oxide.

According to a preferred aspect, the photoactive group is linked to the ethylene groups of units C of the photocrosslinkers by a linking group comprising a phenylene group. Optionally, such a phenylene group is substituted in order to obtain more stability.

According to one embodiment of the invention, the photocrosslinkers comprises substituted ethylene units A, B, C of a macromolecular photocrosslinker in according to:

A= $-CH_2-C(R^1R^2)-$, B= $-CH_2-C(R^1R^3)-$, C= $-CH_2-C(R^1R^4)-$, wherein

R^1 is hydrogen or methyl;

R^2 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group;

R^3 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group when B is $-CH_2-C(R^1R^3)-$ with the proviso that R^2 and R^3 are not the same; and R^4 is $-R^5C(O)P(O)\ R^6R^7$ or $-R^5P(O)R^6OC(O)R^7$, wherein R^5, R^6 and R^7 are selected among same or different aryl groups comprising phenyl, methylphenyl, dimethylphenyl,

trimethylphenyl, methoxyphenyl, dimethoxyphenyl, trimethoxyphenyl, methylolphenyl, dimethylolphenyl, trimethylolphenyl or styryl radicals, or

In the general formula above, -OH denotes a hydroxyl group, Me a methyl group and Ph is a phenyl group. The lactam group typically is a heterocyclic ring structure of 4 to 7 atoms of which at least one is nitrogen. A suitable such lactam group provides a N-vinyl-pyrrolidone structure as one of units A or B on said ethylenic backbone. It is also to be understood that besides the mentioned substituents functional groups for crosslinking can be added to the macromolecule in accordance with conventional methods.

In one advantageous aspect of this embodiment, the photocrosslinkers, R^2 and R^3 according to above are selected so as to form a water-soluble molecule.

Suitable units A and B in the general formula $(A)_n(B)_m(C)_p$ are selected among, but not limited to, N-vinylpyrrolidone (NVP), 2-hydroxyethylmethacrylate, N-N-dimethyl-acrylamide and vinyl acetate. The vinyl acetate referred to preferably will be hydrolyzed conventionally to vinyl alcohol. It is also referred to Table 1 below in the exemplifying part of the description for a number of specific photocrosslinkers based on such units (or co-monomers) and 4-vinylbenzoyl-diphenylphosphine oxide (VBPO) as a photoinitiating group. Accordingly, VBPO units constitute units C in said general formula above. Some especially suitable water soluble, blue light activated photocrosslinkers according to the present invention comprise NVP together with vinyl acetate units, N,N-dimethylacrylamide units alone or together with 2-hydroxyethylethacrylate units, all combined with VBPO units. These photocrosslinkers demonstrate high conversion rate (monomer to polymer) and suitably high stability in aqueous solution. This type of photocrosslinkers can be prepared by conventional radical polymerization.

According to another embodiment, the photocrosslinkers described above with general formula can comprise units A, B and C which are siloxane monomer units having a formula

$-R_aR_bSiO-$, wherein R_a and R_b in units A and B are selected among lower substituted or unsubstituted alkyl groups, aryl groups and arylalkyl groups. Preferably, at least on of R_a and R_b is an aryl or arylalkylgroup. More preferably R_a and R_b is substituted with one or more fluorine atoms. Alkyl groups in this context means a C_1 to C_{10} alkyl group which is

straight or branched.

According to a preferred aspect of this embodiment the siloxane units comprising substituents in accordance with:

A is $-Si(R^1R^2)-O-$, B is $-Si(R^1R^3)-O-$ and C is $-Si(R^1R^4)-O-$, wherein

R^1 is C1 to C6 alkyl; R^2 is C1 to C6 alkyl or phenyl; R^3 is R^1, R^2 or C1 to C6 fluroalkyl;

R^4 is $-R^5R^6C(O)P(O)\ R^7R^8$ or $-R^5R^6P(O)R^7OC(O)R^8$, wherein R^5 is a spacing group; R^6, R^7 and R^8 are selected among same or different aryl groups comprising phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, methoxyphenyl, dimethoxyphenyl, trimethoxyphenyl, methylolphenyl, dimethylolphenyl, trimethylolphenyl or styryl radicals.

The aliphatic spacing group R^5 is preferably comprises between one and ten atoms and suitably

The spacing group is $(-CH_2)_n$, wherein n is between 1 and 10.

According to an aspect of the invnetion particularly suitable for the production of ophthalmic lenses, the photocrosslinkers has radicals connected to the polysiloxane backbone such that R^1 is methyl; R^2 is methyl or phenyl; and R^3 is R^1, R^2 or $-CH_2CH_2CF_3$. Such polysiloxane photocrosslinkers may have functional acrylic groups in its terminal ends. Polysiloxanes of this type and their applicability and advantages, especially for injectable intraocular lenses, are disclosed in the International Patent Application PCT/EP99/07781 which document herewith is incorporated as a reference.

The present invention further involves a method of forming a macromolecular crosslinked network from a fluid composition comprising photocrosslinkers according to any of the mentioned embodiments by irradiating said composition with light exceeding a wavelength of about 305 nm for a time sufficient to form a solid article. The composition can comprise said

photocrosslinkers at least one copolymerizable vinylic, acrylic or methacrylic monomer,

or the composition can comprise a polymer provided with functional vinylic, acrylic or methacrylic groups. It would be obvious to the skilled person to combine any such monomers and polymers together with the inventive photocrosslinkers and also, if found advantageous, combining the composition with a conventional crosslinker suitable for the specifically selected composition. It is further to be understood that the constituents of such a composition shall be selected so as be sufficiently compatible to each other and the selected fluid environment, for example depending on if photocrosslinkers having ethylene or polysiloxane backbone are selected.

In an especially advantageous application of the method, a medical device or medical implant, such an ophthalmic lens is produced by means of a conventional molding method wherein the photocrosslinking into a network is a conventional curing process. The inventive method is particularly suitable for producing an intraocular lens by means of injection and subsequent photocrosslinking direct in the capsular bag of eye, from which the natural lens has been surgically removed.

It is also a part of the present invnetion provide an ophthalmically acceptable composition comprising the new photocrosslinkers. Such a composition will typically have a refractive index greater than about 1.39 and a viscosity such that said composition can be injected through standard cannula having a needle of 15 Gauge, or finer. Such a composition can further comprise of any suitable constituents as outlined above that can be a part of the network provided by the subsequent photocrosslinking.

The photocrosslinkers according to the present invention provide for a combination of photoinitiating and crosslinking processes. It is an important feature of the present invention to effect this combination of function by attaching photoactive groups to a polymeric or macromolecular structure. The photoactive groups, when exposed to light of the appropriate wavelength, will undergo photoinduced scission and generating radicals, which are retained on the polymeric or macromolecular structure. These retained radicals then initiate, terminate, or, in some other way participate in the gel forming process that is the objective of the radiation cure of the photomaterial. The use of the inventive photocrosslinkers confers distinct advantages, both chemical and environmental, as compared with the combination of a separate photoinitiator and crosslinker. In a chemical

context the use of a photocrosslinker gives opportunities to produce networks that are more homogeneous than those produced by photocuring conventional photocurable systems. The latter systems, involving as they do, combinations of monomers, have structures dependent on the reactivity ratios of the monomers and crosslinkers. Often, for example, in a coating being manufactured at high rates of production, a crosslinker is selected because of its high reactivity. Disparities in the reactivates of the components of a formulation gives rise to compositional drift, the change of the average unit composition during the course of a polymerization, and this in relation to a reactive crosslinker implies that sections of a network forming later, in the curing process, have a lower crosslink density than sections formed earlier. Improving the homogeneity of crosslinked networks is a subject receiving greater attention as the technical demands imposed on industrial products increases. Homogenous networks have, for example, higher fracture toughness and better optical properties heterogeneous networks. The shrinkage occurring during their formation is more uniform allowing for more precision in castings. The benefits of using a photocrosslinker as a network former, as compared with a combination of photoinitiator and crosslinker, arise because the radical species they produce act as crosslinkers *via* the polymer chain to which they are attached. Further such radicals are generated throughout the setting phase, their concentration being controlled by the photoinitiating species' quantum efficiency and the intensity of the light, which may be modulated during the setting, in addition to its concentration. This distinction results in the formation of networks having a more controlled and homogeneous structure.

Retaining photoinitiator residues in the network of a medical product, such as a contact lens or a dental filling has desirable physiological implications. Further photocrosslinkers because of their polymeric, or macromolecular, nature are more acceptable, environmentally, than many conventional crosslinkers which are known to cause skin and lung irritation.

Within the context of the present invention, it is possible to substitute a photocrosslinker, either completely, or partially, for a combination of a conventional photoinitiator and a conventional crosslinker. Alternatively, the inventive

photocrosslinkers can be used in combination with a conventional photoinitiator or a conventional crosslinker, as will be understood by practitioners skilled in formulating systems for crosslinking.

Persons skilled in this art will also appreciate that the inventive photocrosslinkers as described herein for photoactive systems responsive to visible light may be applied equally to systems responsive to UV light, so the present invention is of very general applicability.

Detailed and exemplifying description of the invention

Example 1

PHOTOCROSSLINKER POLYMER PREPARATIONS

Table 1

photocrosslinkers	VBPO (mole%) [1]	Comonomer 1 (mole%)	Comonomer 2 (mole%)
P31-1	3.5	HEMA(5)	NVP(91.5)
P32-1	3.5	VAc(10)	NVP(86.5)
P40-3	4	DMA(96)	none
P40-4	4	PEMA(96)	none
P41-1	6	DMA(94)	none

The following Examples describe the preparation of P32-1(3), P40-3 & P41-1 (comparison), and P40-4 respectively. In addition examples demonstrating photocrosslinkers of DMA and 4-vinyl-2,6-dimethylcbenzoylphosphine oxide are added (Examples 1E and 1F).

Example 1A

Photocrosslinker Copolymer employing N-Vinylpyrrolidone and Vinyl acetate

This preparation, on an 8g monomer scale, used monomers in the molar ratio: 86.5 parts N-vinylpyrrolidone (VP): 10 parts vinyl acetate (Vac): 3.5 parts vinylbenzoyldiphenylphosphine oxide (VBPO).

Methoxydiphenylphosphine, 0.520g, was weighed to a dried 100ml twin-neck flask, with one neck septum sealed, and coated in aluminium foil to exclude light. Toluene, 3 ml, and a magnetic stir bar were added and the flask flushed with dry nitrogen. The stopcock was briefly removed and 4-vinylbenzoyl chloride, 0.409g, added, the flask being again flushed with dry nitrogen, then placed in a bath at 65°C, with magnetic stirring.

After 15 minutes, the other monomers: VP, 6.620g, and Vac, 0.595g, were diluted with a previously prepared solution of azobisisobutyronitrile (AIBN), 0.080g in 8ml toluene, and the mixture injected to the flask and rinsed in with a further 4ml toluene. The polymerization mixture was heated at 65°C with magnetic stirring for 8 hours, yielding a clear pale yellow solution, which was precipitated, in subdued light, to diethyl ether. The supernatant was discarded and the pale sludge-like precipitate taken up in 30ml methanol and reprecipitated to ether as a curdy precipitate. The supernatant was decanted, and the polymer product dried to constant weight under vacuum at 35°C . Yield was 5.751g (72%) of friable pale yellow polymer. Elemental analysis gave 0.65% P, corresponding to 6.9%ww VBPO units (0.209mmol/g), and 10.70% N, corresponding to 84.5%ww VP units, and thus a mean unit mass of 115 Daltons. SEC gave Mn 32,000 , Mw 103,000. This implies a number average chain length of ca.280 units, with ca.7 photoactive units per chain.

Example 1B

Photocrosslinker Copolymer employing N-Dimethylacrylamide (I)

In this example, 4-vinylbenzoyldiphenylphosphine oxide (VBPO), 4 mol%, was copolymerized with N,N-dimethylacrylamide (DMA), 96 mol%, on a 6g scale.

Methoxydiphenylphosphine, 0.481g, was weighed to a dried 24x150mm Quickfit tube, and 2.5ml dry toluene added. The tube was then wrapped in aluminium foil to exclude light. 4-Vinylbenzoyl chloride, 0.368g, and a magnetic stir bar were added, and the tube septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes a solution of DMA, 5.26g, and AIBN, 0.060g, in toluene, 5ml, was injected by

syringe and rinsed in with a further 3.6ml toluene. The mixture was stirred 6h at 65°C, yielding a viscous orange-yellow solution, which was diluted with methanol and precipitated in diethyl ether. The product was reprecipitated from methanol to ether, and vacuum dessicated at room temperature. Yield, 2.56g (43%) of friable pale yellow polymer, analysis 0.82% P corresponding to 8.8%ww VBPO units (0.265mmol/g). GPC using poly(ethylene glycol) standards gave Mn 25,000; Mw 100,000 .

Example 1C

Photocrosslinker Copolymer employing N-Dimethylacrylamide (II)

Example 2B was repeated on a 12 g scale, but with monomer ratio 6 mol% VBPO (2.12 g), 94 mol% DMA (9.89 g), with 0.120 g AIBN, 22.3 ml toluene, and polymerization time extended to 8h at 65°C. The yield was 7.17g (60%) of yellow polymer, analysis 1.49% P corresponding to 16.0 %ww VBPO (0.481mmol/g).GPC gave Mn 12 000 and Mw 88000.

Example 1D

Photocrosslinker Copolymer employing 2-Phenylethyl methacrylate

In this example, 4-vinylbenzoyldiphenylphosphine oxide (VBPO), 4 mol%, was copolymerized with 2-phenylethyl methacrylate (PEMA), 96 mol%, on a 6g scale.

Methoxydiphenylphosphine, 0.271g, was weighed to a dried 24x150mm Quickfit tube, and 2.5ml dry toluene added. The tube was then wrapped in aluminium foil to exclude light. 4-Vinylbenzoyl chloride, 0.204g, and a magnetic stir bar were added, and the tube septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes a solution of PEMA, 5.60g, and AIBN, 0.060g, in toluene, 5ml, was injected by syringe and rinsed in with a further 3.6ml toluene. The mixture was stirred 6h at 65°C, yielding a fairly viscous pale yellow solution, which was diluted with chloroform and precipitated to methanol. The product was reprecipitated from chloroform (with THF

added to clarify the solution), and vacuum dessicated at room temperature. Yield, 4.67g (78%) of friable pale yellow polymer, analysis 0.48% P corresponding to 5.2%ww VBPO units (0.155mmol/g). GPC in THF using polystyrene standards gave Mn 49,300; Mw 108,500 .

Example 1E

In this example, 4-vinyl-2,6-dimethylbenzoyldiphenylphosphine oxide (VDMBPO), 4 mol%, was copolymerized with N,N-dimethylacrylamide (DMA), 96 mol%, on a 12g scale.

Methoxydiphenylphosphine, 0.979g, was weighed to a dried flask and 5ml dry toluene added. The flask was wrapped in aluminium foil to exclude light. 4-Viny-2,6-dimethyllbenzoyl chloride, 0.885g, and a magnetic stir bar were added, and the flask septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes a solution of DMA, 10.426g, and AIBN, 0.121g, in toluene, 9.3ml, was injected by syringe and rinsed in with a further 8ml toluene. The mixture was stirred 8h at 65°C, yielding a viscous pale yellow solution, which was diluted with 20ml ethanol and precipitated in diethyl ether. The product was reprecipitated from ethanol to hexane, and vacuum dessicated at room temperature. Yield, 8.53g (71%) of friable pale yellow polymer, analysis 0.58% P corresponding to 6.75%ww (1.95mol%) VDMBPO units (0.187meq/g).

The polymer was water soluble and showed excellent hydrolytic stability; tested over the course of a year the product showed no measurable decrease in photoactivity. GPC gave Mn 6,000; Mw 26,000 .

Example 1F

Example 1E was repeated employing VDMBPO 5 mol and DMA 95 mol%. Yield was 43% of pale yellow polymer, analysis 0.86% P corresponding to 10.0%ww (2.97mol%) VDMBPO units (0.278meq/g). GPC gave Mn 7,000; Mw 32,500.

Example 1G

Example 1F was repeated employing VDMBPO 5 mol% and DMA 95 mol%. Yield was 55% of pale yellow polymer, analysis 0.73% P corresponding to 8.5%ww (2.49mol%) VDMBPO units (0.236meq/g). GPC gave Mn 5,600; Mw 24,000.

EXAMPLE 1H

1,3,5-trimethylbenzoyl-styrylphenylphosphine oxide (TMBSPO), 4 mol%, was copolymerized with N,N-dimethylacrylamide (DMA), 96 mol%, on a 12g scale.

First methoxystyrylphenylphosphine, 0.800g, was weighed to a dried flask and 5ml dry toluene added. The flask was wrapped in aluminium foil to exclude light. 1,3,5-trimethyllbenzoyl chloride, 1.061g, and a magnetic stir bar were added, and the flask septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes subsequently a solution of DMA, 10.241g in 15 mL of toluene, and AIBN, 0.120g in 5.0 mL of toluene, were injected by syringe. The mixture was stirred 8h at 65°C, yielding a viscous pale yellow solution, which was diluted with 20ml ethanol and precipitated in diethyl ether. The product was reprecipitated from ethanol to diethylether, and vacuum dessicated at room temperature. Yield was 55% of pale yellow polymer, analysis 0.87% P corresponding to 10.4%ww (2.40mol%) TMBSPO units (0.227meq/g). GPC gave Mn 9,000; Mw 35,000.

The experiment was repeated employing TMBSPO 2.5 mol% and DMA 97.5 mol%. Yield was 79% of pale yellow polymer, analysis 0.43% P corresponding to 5.1%ww (1.19mol%) TMBSPO units (0.112meq/g). GPC gave Mn 15,000; Mw 94,000.

Finally, the experiment was repeated employing TMBSPO 4 mol% and PEMA 96 mol%. Yield was 68% of friable pale yellow polymer, analysis 0.56% P corresponding to 5.4%ww TMBSPO units (0.149mmol/g). GPC gave Mn 19,000 and Mw 165,000.

Example 2

The following examples refer to photopolymerization including the inventive photocrosslinkers compared with photopolymerization with commercially available photoinitiators.

Example 2A

The state of the art photoinitiator Irgacure 1800 (ex Ciba-Geigy, 10.0 mg) was dissolved, in subdued light, in 2-hydroxyethylmethacrylate (HEMA, ophthalmic grade ex Polysciences, 970 mg) and 1,6-dihydroxyhexane diacrylate (HDDA, ex, 20.0 mg), and a 10.0 mg sample pipetted into an open DSC aluminum sample pan. The sample pan, covered with a cover-slip of thin glass, was placed in the sample position of the head of a TA Instruments Differential Photocalorimeter (DPC). The temperature of the head was allowed to stabilize under N_2 at 37°C (or in some cases 23°, and the sample irradiated with blue light at an intensity of 8-9 $mWcm^{-2}$.

The area of the polymerization exotherm was determined by conventional computation and the Jg^{-1} of monomer calculated. From the Jg^{-1} the percentage conversion of monomer to polymer was calculated using a literature value for the latent heat of polymerization of the monomer, ΔH_p. The findings are collected in Table 2.

Using the same composition as was used for the DPC tests discs (2mm thick x 16mm diameter) of polyHEMA were cast in PTFE casting cells. About 500mg of the mixture of monomers and photoinitiator were introduced into the cell which was closed with a glass slide and irradiated with blue light, either from a blue light dental gun, or from a proprietary light generator (Efos Novacure), for 3min.

Example 2B

The method described in Example 2A was repeated using with the state of the art photoinitiator Lucirin TPO (ex BASF, 10.0mg) instead of Irgacure 1800.

Example 2C

The method described in Example 2A was repeated using HEMA (900.0mg), no HDDA, and, instead of Irgacure 1800, a photocrosslinker according to the present invention (P31-1, see Table1. for composition, 100.0mg)

Example 2D

The method described in *Example 2*C was repeated using a photocrosslinker according to the present invention (P32-1, see Table 1. for composition, 100.0mg).

Example 2E

The method described in *Example 2*C was repeated using a photocrosslinker according to the present invention (P40-3, see Table 1. for composition, 100.0mg).

Example 2F

The method described in *Example 2C* was repeated using a photocrosslinker according to the present invention (P41-1, see Table 1. for composition, 100.0mg).

Example 2G

The method described in *Example 2A* was repeated using a photocrosslinker according to the present invention (P32-1, 100.0mg) instead of Irgacure 1800, HEMA (600.0mg),

water(300mg) and no HDDA.

Example 2H

As *Example 2G*, using P40-3 (50.0mg) to replace P32-1, and HEMA (500.0mg), water (450.0mg).

Example 2I

As *Example 2H* using P41-1(50.0mg) to replace P40-3.

Example 2J

The method described in *Example 2A* was repeated using 2-phenylethylacrylate (PEA, 990.0mg, ex Polymer & Dajac Laboratories) instead of HEMA and no HDDA.

Example 2K

The method described in *Example 2A* was repeated using instead of Irgacure 1800 a photocrosslinker (P40-4, see Table 1. for composition, 100.0mg) and PEA (900mg) but no HDDA or HEMA.

The % conversions of monomer to polymer in Table 2., Examples 2A and 2B, the commercial photoinitiators, and the photocrosslinkers, Examples 2C to 2E, are comparable showing that the photocrosslinkers behave as efficient photoinitiators, especially giving regard to the concentrations of photoactive species, the acylphosphine oxide (shown in Table 1) Further when these findings are compared with Examples 2G to 2I the comparison reveals that correctly designed photocrosslinkers (Examples 2H and 2I) exhibit 100% conversions in solution in water.

For the 2-phenylethylacrylate monomer the photocrosslinker P40-4, based on 2-phenylethylmethacrylate, is also very efficient as a photoinitiator (comparing Examples 2J and 2K) giving 100% conversion of monomer to polymer gel, as judged from the heat of polymerization (based on experimentally determined ΔH_p).

Table 2. A comparison of the completeness of blue light photopolymerisation of HEMA, HEMA in water, & PEA using low molecular weight photoinitiators and photocrosslinkers

Ex. No.	**Formulation**[a] (wt%)[m.eq photoactive ingredient[b]/100g]	**Heat of Polym.** (Jg^{-1})	**Polym. time** (min)	**Conversion** %
2A	HEMA(97)HDDA(2)I1800(1)[0.51]	351	3.5	80
2B	HEMA(97)HDDA(2)TPO(1)[2.9]	357	1.5	82
2C	HEMA(90)P31-1(10)[2.0]	308	6	70
2D	HEMA(90)P32-1(10)[2.3]	309	3	71
2E	HEMA(90)P40-3(10)[2.7]	307	2	70
2F	HEMA(90)P41-1(10)[4.8]	361	1.5	82
2G	HEMA(60)H_2O(30)P32-1(10)[2.3]	>275	>7	>63
2H	HEMA(50)H_2O(45)P40-3(5)[1.4]	452	7	100(approx.)
2I	HEMA(50)H_2O(45)P41-1(5)[2.4]	454	6	100(approx.)
2J	PEA(99)I1800(1)[0.51]	455	2.5	100(approx.)
2K	PEA(90)P40-4(10)[1.6]	456	3.5	100(approx.)

[a]Photocrosslinkers, and monomer HEMA, as Table 1.: commercial photoinitiators

I1800, bis(2,6-dimethoxybenzoyl)-trimethylpentylphosphine oxide (25%) + 1-hydroxy-cyclohexylphenylketone (75%)(Irgacure 1800 ex Ciba-Geigy)
TPO, 1,3,5-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO ex BASF):
monomer PEA, 2-phenylethylacrylate: crosslinker HDDA, hexan-1,6-diol diacrylate
[b]m.eq. of acylphosphine oxide/100g of formulation.

Example 3

Examples for Gelation Tests:

Examples 3A and 3B

Using the formulations described above in Examples 2J and 2K and the casting method described in *Example 2A* discs were prepared.

Example 3C

Irgacure 2959 (ex Ciba-Geigy, 10.0 mg) was dissolved, in subdued lighting, in 2-hydroxyethylmethacrylate (HEMA, ophthalmic grade ex Polysciences, 550.0 mg) and water (440.0 mg). Test discs (2mm thick x 16mm diameter) of polymer were cast in PTFE casting cells. About 800mg of the mixture of monomers and photoinitiator were introduced into the cell which was closed with a glass slide and irradiated with light from a proprietary light generator (Efos Novacure), for 3 min.

Example 3D

As *Example 3C* with Irgacure 2959 (30.0 mg), HEMA (540.0 mg) and water (430.0 mg).

Example 3E

As *Example 3C* with P40-3 (100.0 mg) replacing Irgacure 2959, HEMA (500.0mg), and

water (400.0mg).

Example 3F

As *Example 3C* with P41-1 (70.0mg) replacing Irgacure 2959, HEMA (510.0mg), and water (420.0mg).

Example 3G

As *Example 4C* with P40-4 (50.0mg) replacing Irgacure 1800, PEA (900.0mg), and additional crosslinker, CE7-2 (2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate copolymer [0.9:0.1 mole ratio], 50.0mg).

Example 3H

As *Example 3G* with Irgacure 1800 (21.0mg) replacing P40-4, PEA (940.0mg), and crosslinker, CE7-2 (2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate copolymer [0.9:0.1 mole ratio], 60.0mg).

Example 3I

As *Example 3B* with PEA (750.0mg), and photocrosslinker, P40-4 (250.0mg).

In Table 3. are collected the tests made to check the gelation of the different formulations. Where a composition is gelled it does not dissolve in solvent, but swells to an extent related to its crosslink density. Uncrosslinked (sol) polymers dissolve.

Examples of monomers photopolymerized with conventional photoinitiators of low molecular weight, nos. 4A, 4C and 4D dissolved readily in the appropriate solvent, water for polyHEMA, and acetone for polyPEA. Example no. 4B showed an intermediate

behavior and dissolved partially in acetone leaving some residual gel. Increasing the proportion of photocrosslinker to 25% (3.9m.eq. of acylphosphine oxide, Example 4I or, adding separate crosslinker, CE7-2 (Example 4G, see below) produced acetone insoluble gel.

CE7-2, a polyPEMA which is unsaturated and PEA miscible, being a copolymer of 2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate [0.9:0.1 mole ratio], was employed as a supplementary crosslinker to the photocrosslinker P40-4, in Examples 4G and 4H. That CE7-2 is an effective cross-linker for photopolymerized PEA is demonstrated in example no. 4H, where in combination with Irgacure 1800 it also yields a gelled product upon irradiation. The products upon irradiation are transparent gelled elastomers of high refractive index (RI>1.54), similar in properties to PEA/PEMA copolymers.

Examples 3E and 3F which used photocrosslinkers to replace conventional photoinitiators for HEMA/water compositions were gelled and did not dissolve in water, unlike examples 4D and 4E.

Table 3. Gelation tests on photopolymerized materials, shewing effect of photocrosslinkers

Ex. No.	Formulation (wt%)[1]	Effect of Solvent	Comments
3A	PEA(99)I1800(1)	Dissolves in Acetone	Not Crosslinked
3B	PEA(90)P40-4(10)	Dissolves & Swells in Acetone	Lightly Crosslinked
3C	HEMA(55)H_2O(44)I2959[2](1)	Dissolves in Water	Not Crosslinked
3D	HEMA(54)H_2O(43)I2959(3)	Dissolves in Water	Not Crosslinked
3E	HEMA(50)H_2O(40)P40-3(10)	Swells in Water	Crosslinked Gel

3F	HEMA(51)H_2O(42)P41-1(7)	Swells in Water	Crosslinked Gel
3G	PEA(90)CE7-2(5)P40-4(5)	Swells in Acetone	Crosslinked Gel
3H	PEA(94)CE7-2(6)I1800(2.1)	Swells in Acetone	Crosslinked Gel
3I	PEA(75)P40-4(25)	Swells in Acetone	Crosslinked Gel

[1] See Tables 1. & 2., and text for an explanation of materials codes

[2]I2959, 2-hydroxy-4'-hydroxyethoxy-2-propiophenone (UV curing)

The crosslinked structure of the water swollen hydrogels (4E and 4F) was confirmed by stress relaxation tests.

Example 4

The method described in Example 2A was repeated using the following formulations:

Formulations (wt %)

4A. water (80)/photocrosslinker according Example 1F(20)

4B. water (80)/photocrosslinker according Example 1H(20)

4C. HEMA(45)/water(35)/photocrosslinker according to Example 1C(20)

4D. HEMA(45)/water(35)/photocrosslinker according to Example 1F(20)

4E. HEMA(45)/water(35)/photocrosslinker according Example 1H(20)

4F. HEMA(45)/H20(35)

The coherent and clear gels resulted from the irradiation of the formulations with blue light, and their relative crosslinked nature was characterized in two ways. The first method was to measure the stress relaxation of the networks, using a Rheometrics RDA-11, and the second method used was to measure the smiling of the gels in water.

Stress Relaxation Tests-Method

The RDA-11 was set up with the 16mm gelled sample damped between parallel plates of 25 mm, heated to 35°C, and a strain of 30% applied. During the test the instrument measures the instantaneous stress necessary to maintain 35%, and plots the instantaneous shear modulus (Gi) against log t. In Table 3, the percentage reductions in the modulus Gi for the formulations 4A to 4F between i = 10 and 100 s are compared as (G(10) – G(100)/G(10))x100 both before and after swelling in water. The results confirm that the photocrosslinked gel possess coherent network structures.

Table 3. Average Stress Relaxations of Photocrosslinked Formulations 4A to 4F, measured at 35°C

Average stress relaxation	4A	4B	4C	4D	4E	4F
Before swelling-disc1	No result		4.9	3.4	No result	Not measurable
Before swelling-disc2	9.3		15.5	10.9	29.4	
After swelling-disc1			21.4	17.4		
After swelling-disc2	19.1		19.0	13.0	12.4	Not measurable

Swelling Test Method

Samples discs from formulations 4A through 4F were weighed, immersed in water for 24 hours at 20°C, dried, and reweighed. Table 4 compares the water absorbed by each formulation on a percentage basis.

Table 4.

Percentage water absorbed at 25°C by photocrosslinked gels

Water absorbed (wt %)	4A	4B	4C	4D	4E	4F
Disc1			222	191		Not measurable
Disc2	130	219	230	172	255	Not measurable

It was observed that upon irradiation with blue light, the formulation prepared without a crosslinker (4F) did not gel and that no discs suitable for any measurements were formed. Satisfactory discs were prepared from other formulations and stress relaxation results and the water absorption results were in agreement with the sequence: most highly crosslinked 4A>4C<4E least highly crosslinked.

Claims

1. Macromolecular photocrosslinkers having a general formula

$(A)_n(B)_m(C)_p$, wherein

(i) A, B and C are units of substituted ethylene or siloxane groups in the macromolecular structure;

(ii) C carries a photoactive groups;

(iii) n = 0-98 mole %, m = 0-98 mole %, n+m = 50-98 mole % and p = 0.5-50 mole %;

and when said photoactive groups are exposed to light of determined wavelengths above 305 nm, radicals are generated and retained on the macromolecular photocrosslinkers and reacting so as to accomplish a crosslinked network structure.

2. Photocrosslinkers according to claim 1 characterized in that said photoactive group comprises a phosphine oxide.

3. Photocrosslinkers according to claim 2 characterized in that the photoactive group is an acyl- or aroyl phosphine oxide.

4. Photocrosslinkers according to claim 3 characterized in that the photoactive group is linked to the ethylene groups of units C by a linking group comprising a phenylene group, said phenylene group being optionally substituted.

5. Photocrosslinkers according to claim 1, wherein the ethylene units A, B, C of the macromolecular structure comprises substituents in accordance with:

A= $-CH_2-C(R^1R^2)-$, B= $-CH_2-C(R^1R^3)-$, C= $-CH_2-C(R^1R^4)-$, wherein

R^1 is hydrogen or methyl;

R^2 is -CON(Me)$_2$, -$CO_2CH_2CH_2OH$, -$OCOCH_3$, -$OCOCH_2CH_2Ph$, -OH or a lactam group;

R^3 is -CON(Me)$_2$, -$CO_2CH_2CH_2OH$, -$OCOCH_3$, -$OCOCH_2CH_2Ph$, -OH or a lactam group when B is -CH_2-$C(R^1R^3)$- with the proviso that R^2 and R^3 are not the same unless R^2 and R^3 is -OH ; and
R^4 is -$R^5C(O)P(O)$ R^6R^7 or –$R^5P(O)R^6OC(O)R^7$, wherein R^5, R^6 and R^7 are selected among same or different aryl groups comprising phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, methoxyphenyl, dimethoxyphenyl, trimethoxyphenyl, methylolphenyl, dimethylolphenyl, trimethylolphenyl or styryl radicals.

6. Photocrosslinkers according to claim 5, wherein R^2 and R^3 are selected so as to form a water-soluble molecule.

7. Photocrosslinkers according to claim 5, wherein said lactam units together with units A or B constitute N-vinylpyrrolidone units.

8. Photocrosslinkers according to claim 5, wherein at least one of R^2 and R^3 is hydroxyl.

9. Photocrosslinkers according to claim 5, wherein A is N-vinylpyrrolidone, B is vinyl alcohol.

10. Photocrosslinkers according to claim 1 or 5 provided with functional groups for crosslinking.

11. Photocrosslinkers according to claim 10 provided with functional groups selected among vinylic, acrylic and methacrylic groups.

12. Photocrosslinkers according to claim 1 characterized in that units A, B and C are

siloxane monomer units of a general formula $-R_aR_bSiO-$, wherein R_a and R_b in units A and B are selected among lower substituted or unsubstituted alkyl groups, aryl groups and arylalkyl groups.

13. Photocrosslinkers according to claim 12, wherein at least on of R_a and R_b is an aryl or arylalkylgroup.

14. Photocrosslinkers according to claim 13, wherein at least one of R_a and R_b is substituted with one or more fluorine atoms.

15. Photocrosslinkers according to claim 1, wherein units A, B, C are siloxane units comprising substituents in accordance with:

A is $-Si(R^1R^2)-O-$, B is $-Si(R^1R^3)-O-$ and C is $-Si(R^1R^4)-O-$, wherein

R^1 is C1 to C6 alkyl; R^2 is C1 to C6 alkyl or phenyl; R^3 is R^1, R^2 or C1 to C6 fluroalkyl;

R^4 is $-R^5R^6C(O)P(O)\ R^7R^8$ or $-R^5R^6P(O)R^7OC(O)R^8$, wherein R^5 is a spacing group; R^6, R^7 and R^8 are selected among same or different aryl groups comprising phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, methoxyphenyl, dimethoxyphenyl, trimethoxyphenyl, methylolphenyl, dimethylolphenyl, trimethylolphenyl or styryl radicals.

16. Photocrosslinkers according to claim 15, wherein R^5 is aliphatic spacing group comprising between one and ten atoms.

17. Photocrosslinker according to claim 16, wherein said spacing group is $(-CH_2)_n$, wherein n is between 1 and 10.

18. Photocrosslinkers according to claim 15, wherein R^1 is methyl; R^2 is methyl or phenyl; R^3 is R^1, R^2 or $-CH_2CH_2CF_3$.

19. Photocrosslinkers according to claim 15 having functional acrylic groups in its terminal ends.

20. A method of forming a macromolecular crosslinked network from a composition comprising a photocrosslinker according to any of claims 1 to 19 by irradiating said composition with light exceeding a wavelength of about 305 nm for a time sufficient to form a solid article.

21. A method forming a macromolecular crosslinked network from a composition comprising a photocrosslinker according to any of claims 1 to 11 and at least one copolymerizable vinylic, acrylic or methacrylic monomer.

22. A method according to claim 20, wherein said composition further comprises a polymer provided with functional vinylic, acrylic or methacrylic groups.

23. A method according to claim 22, wherein said polymer has a backbone of ethylene units.

24. A method according to claim 22, wherein said polymer is a polysiloxane.

25. A method according to any of claims 20 to 24, wherein an ophthalmic lens is produced.

26. A method according to claim 25, wherein an intraocular lens is produced in the capsular bag of the eye.

27. An ophthalmically acceptable composition comprising photocrosslinkers according to any of claims 1 to 19, having a refractive index greater than about 1.39 and a viscosity such that said composition can be injected through standard cannula having a needle of 15 Gauge, or finer.

28. The use of photocrosslinkers according to any of claims 1 to 19 in an ophthalmologically acceptable composition for injection into the capsular bag of the eye.

INTERNATIO SEARCH REPORT

Int. tional Application No
PCT/EP 00/02539

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F8/00 C08G77/38 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	L. ANGIOLINI: "POLYMERIC PHOTOINITIATORS BEARING SIDE-CHAIN BENZOYLDIPHENYLPHOSPHINOXIDE MOIETIES FOR UV CURABLE COATINGS" JOURNAL OF APPLIED POLYMER SCIENCE, vol. 51, no. 1, 3 January 1994 (1994-01-03), pages 133-143, XP000464122 NEW YORK, US page 133 -page 143	1-14
Y	WO 92 09644 A (BAUSCH & LOMB INC.) 11 June 1992 (1992-06-11) page 6, line 1 - line 21; claims 1-30	1-32
Y	WO 92 07885 A (BIOCOMPATIBLES LTD.) 14 May 1992 (1992-05-14) claims 1-16	1-32

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2000	16/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Permentier, W

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 661 195 A (R. CHRIST) 26 August 1997 (1997-08-26) column 7, line 17 - line 34; claims 1-14	1-32
Y	WO 99 08135 A (ALCON LABORATORIES, INC.) 18 February 1999 (1999-02-18) page 4, line 5 - line 14 page 5, line 4 - line 30 page 6, line 2 - line 14 page 7, line 7 - line 21 page 7, line 32 -page 8, line 7 page 9, line 10 - line 25; claims 1-15	1-32
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F8/00 C08G77/38 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2000	16/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Permentier, W

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